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(57) Abstract

The present invention relates to a particulate filter material that is devoid of any and all respirable silica consisting of rice hull ash (RHA) and the method for making the same. The invention also relates to the clarification and decoloring of mono–, di–, and trisaccharides using the RHA particulate filter material. The present invention also relates to a RHA filter material that may contain both polar and non–polar constituents.

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CLARIFICATION OF CARBOHYDRATE HYDROLYSATES

PRIORITY OF INVENTION

This application claims priority under 35 U.S.C. §119(e) from U.S. Provisional Application Number 60/120,755, filed February 18, 1999.

FIELD OF THE INVENTION

The present invention relates to a particulate filter material consisting of rice hull ash (RHA) and the method for making the same. The invention also relates to the clarification and decoloring of mono-, di-, and trisaccharides using the RHA particulate filter material. The filter composition of the present invention has the specific characteristic that it is devoid of any and all respirable silica detailed by the Occupational Safety and Health Administration (OSHA) as being carcinogenic. Such materials are, by way of illustration, cristobalite and tridymite. The present invention also relates to a RHA filter material that may contain both polar and non-polar constituents.

BACKGROUND OF THE INVENTION

The conversion of complex carbohydrates to monosaccharides for use in the food industry requires clarification and decolorization to improve acceptability. Various filtration aids are utilized such as diatomaceous earth and other mined products that assist the filtration. Separate bleaching agents such as activated carbon are also used.

It has been known to use absorbent and adsorbant filter materials for the process of removing impurities from liquids, and more particularly from liquid food, and chemical compositions. In these applications the filter aid material (FAM) has been known to consist of mined products: diatomaceous earth, perlite, zeolites, bentonite, zirconium oxide, activated charcoal, activated alumina, and ferrous sulfide;

fibers such as: cellulose, teflon, nylon, rayon, PVC, and PPL; agricultural waste products such as: calcined sugar cane bagasse, corn cobs, peanut shells, wheat straw, oat straw, rice straw, rice hulls, cottonseed hulls, and paper from cotton or wood; chemical decoloring agents such as hydrogen peroxide. While these FAMs are effective and useful in reducing color and impurities from liquids, they may contain respirable carcinogenic materials that require special handling, thus increasing the cost of using such FAMs. RHA is used to a limited extent as FAMs. The calcining conditions for rice hulls generally produce the carcinogens cristobalite and tridymite in amounts that exceed the existing specification of being less than or equal to 0.01%. Silica products containing cristobalite and tridymite in excess of this amount require special breathing apparatus for employees exposed to such products.

U.S. Patent No. 5,360,633 describes the treatment of RHA with a coating of vegetable oil and/or glyceride to minimize the amount of respirable particles. Diatomaceous earth (DE), a common FAM, is composed of about 90% calcined silicon dioxide and contains up to 65% cristobalite, far in excess of the OSHA specification.

Large quantities of FAMs are in great demand for decoloring and removing the turbidity from such liquids as sugar liquors. Approximately 240 million pounds of FAM are used annually in this applicatoin alone and there is a constant demand for more cost effective and efficient ways to filter these sugar liquors. Patents abound detailing new and ingenious ways to produce better FAMS. U.S. Patent No. 5,194,093 describes a process for decolorization of sugar liquor utilizing hydrogen peroxide. Activated charcoal is a widely used adsorbant which attracts high molecular weight impurities from liquids. It is produced by calcining coal, peat and other agricultural by-products at temperatures between 700-1100°C under a steam, nitrogen or carbon dioxide environment. An admixture of bone char and activated carbon as described in U.S. Patent No. 4,252,571, improves the decolorization of sugar liquors. However, there is a reluctance on the part of many food processors to

use animal remains as an FAM. A sophisticated, high cost process of ultra-filtration or ultra-centrifugation is described in U.S. Patent No. 5,468,301, and consists of a set of packed columns filled with absorbents and/or membranes to decolor sugar liquor. U.S. Patent No. 4,502,890 describes the use of activated carbon for the purification of sugar liquor. U.S. Patent No. 5,281,279 describes the use of activated charcoal (AC) and diatomaceous earth (DE) to filter sugar liquor but not to decolor it. FAMs such as DE and AC are expensive to produce because of the long processing times. DE is often imported, adding to the cost. U.S. Patent No. 4,765,545 describes the production of a rice hull ash. However, it is produced at 900°C which is beyond the tridymite forming temperature. Additionally, the RHA thus produced must be milled and sieved prior to use.

Thus, it would be desirable to have a FAM that is easily manufactured, that shows improved filter rate and clarification of the sugar liquor, is produced at a fraction of the cost of DE and AC and does not contain respirable carcinogenic material. Further, it would be desirable to have the RHA and RSA filter aid materials exhibit both polar and non-polar characteristics simultaneously.

SUMMARY OF THE INVENTION

The present invention describes a filter aid material created by a single controlled burning of rice hulls. The ash filter material of the invention consists of an amount of amorphous silica (AS) equal to $92\% < AS < 100\%$ by weight, and an amount of activated carbon (AC) equal to $0\% < AC < 5\%$ which amounts depend upon the method of preparation. The present invention also discloses the use of RHA to clarify mono-, di-, and trisaccharide liquors, wherein an amount of rice hull ash (RHA) equal to at least 0.1% by weight of the total liquor is added to the liquor, and can contain an amount of RHA equal to 1.0% by weight of the total liquor.

The RHA filter aid material is advantageous because the burning process can produce an ash containing both AS and AC. Additionally, the calcining temperature

is maintained between 650°C and 850°C which is below the tridymite formation temperature of 867°C, and the cristobalite formation temperatuer of 1470°C. The RHA filter material has the added benefit of meeting the respirable specification for amorphous silica published by the regulating agencies such as OSHA.

The rice hulls may be milled or not prior to calcination, or after. This allows the RHA filter aid to possess more or less surface area to enhance either one or both of the filtration variables: through-put rate, and extent of decolorization and/or separation. AC is a non-polar adsorbant which attracts high molecular weight materials, while AS is a polar adsorbant that attracts molecules by means of forces such as electrostatic attraction and hydrogen bonding.

According to the present invention the RHA filter medium may be tailored to remove certain materials from liquids by altering both the AS:AC ratio and the degree to which the filter composition is milled.

Rice hulls are waste products that are burned in high heat furnaces to reduce their bulk prior to disposal in the land-fills. The present invention ashes the rice hulls under controlled and precise conditions to create a high through-put, effective decoloring FAM for sugar liquors that has the added advantage of being more cost effective than other filter media such as AC, and DE.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a graph of temperature vs. weight % on the TGA of milled and unmilled rice hulls.

DETAILED DESCRIPTION

The present invention relates to a FAM for use in liquid food, and chemical processing and relates specifically to sugar liquors. Several processes may be used to

convert complex carbohydrates to mono-, di-, and trisaccharides. These include acid processes, acid combined with enzymes, and enzymatic processes. After conversion, the liquor is clarified, decolorized, and concentrated. The clarification step is necessary to remove traces of insoluble lipids, protein, starches as well as high molecular weight polymers and degradation products created during the conversion. Clarification by filtration and centrifugation is practiced. Use of rice hull ash (RHA) at 0.1 to 1.0% of the liquor enhances the rate of filtration, improves color removal and removal of foreign material from the liquor stream.

This invention also relates to the method of making the FAM. The FAM compositions are comprised of RHA, either milled or not, having an AS and AC composition by weight of 94%<As<100%, and 0%<AC<6%, and cristobalite <0.01%. The rice hulls are incinerated into an ash composition, wherein the resultant ash may contain two products which are effective adsorbants. In the present invention the raw materials are calcined at a temperature of between 300°C and 430°C such that a predominantly amorphous silica ash is produced. Figure 1 shows a thermogravemetric analysis (TGA) performed under the conditions of the present invention on unmilled and milled rice hulls. At temperatures between 60°C and 200°C there is a residual water loss from the hulls of about 10%. The volatiles burn off between 200-300°C. Lignins are incinerated between 300-430°C, resulting in a predominantly silica ash that is between 19-22% of the original weight of the rice hulls. Between 4-7% carbon is contained within the final silica ash. This carbon may be burned off by additional calcining above 430°C for 17 minutes. If desired, the residual 4-7% carbon conatined in the RHA of the present invention may be activated using a phosphoric acid process at a temepratue of between 400-560°C. This science is well known to those skilled in the art. At all times the calcining temperature is kept below 867°C to avoid the formation of carcinogenic tridynite from β-quartz. Figure 1 also shows there is no significant difference in TGA weight loss data between milled and unmilled rice hulls, nor is furnace heating rate a factor. The silica portion of the ash is a polar adsorbant and, as such, interacts with the adsorbed molecules by means

of particular forces such as electrostatic attraction and hydrogen bonding. The activated carbon is a non-polar adsorbant that retains organic compounds with a preference to higher molecular weight compounds and aromatic derivatives. The RHA of this invention has a bulk density between 16-24 lb/cu.ft. and contains particles between 2 millimeters and 0.40 microns in size. The particle size of the RHA can be varied depending upon the extent to which the hulls are milled prior to calcination, or are ground/pulverized after ashing.

The RHA is composed of generally elongated fibers capable of forming a highly permeable mass within which impurities and heavier constituents are trapped. The use of the present invention may be applied to hydrolysate streams from complex carbohydrate conversion processes such as low conversion sugars (corn syrup solids), to preparation of dextrose, to high fructose corn syrup processing. In a typical usage RHA may be sandwiched between sheets of porous material, or made into a filter cake to be placed in the mixture or liquor stream during a continuous process. According to the present invention, the RHA also may be used in loose-powder form for separating, clarifying, filtering, and decolorizing constituents in a batch process. The filter material produced by the method of the present invention is most effective when added to a liquid filtrate in an amount equal to at least 0.05% by weight of the total filtrate and up to an amount equal to 20% by weight of the total filtrate.

Use of the RHA of the present invention for clarification of saccharide mixtures and liquors is advantageous because the RHA can provide an increased rate of filtration relative to DE and other RHAs. The RHA may be manufactured to contain both AC and AS. Many filter applications utilize more than one filter medium over a series of stages. The use of the RHA product described in the present invention may eliminate one or more of the filtering steps.

Not only does the RHA enhance filter through-put, but it also removes more color from sugar liquors than DE and other RHAs. Thus, the sugar liquors clarified by the use of the RHA of the present invention become more desirable final products.

Rice hulls are environmentally difficult to dispose of. The hulls are burned to create waste heat and the ash is usually placed in landfills. The RHA of the present invention is a value-added product instead of waste product. The spent RHA is easily recycled by reincinerating to combust the adsorbed material. It may also be disposed of in a landfill as is currently practiced. Another advantage of using RHA as a separator and clarifier for saccharides is its reduced cost (approximately 60% less) relative to other filter agents, such as diatomaceous earth.

EXAMPLES

The following are examples demonstrating the production and use of RHA for the decoloring of saccharides. It will be appreciated by one skilled in the art that the invention is not limited to the following examples.

Example 1:

Unmilled rice hulls were burned in a gassifier at 800°C for 4 minutes. The resulting ash was assayed and contained by weight 91.91% Silicon Dioxide, and 4.47% Carbon. The ash was size-classified using standard sieves as follows:

Sieve Size	% Retained (by weight)
20	2.57
40	29.74
60	39.28
80	15.83
100	4.12
120	2.99
140	1.91
170	1.02
bottom pan	2.54

The residual carbon was burned off using a Thermolyne Model F-A1730 muffle oven at 800°C. The weight loss during this second ashing was 4.4% which corresponded to the amount of carbon remaining after the first incineration. An assay of the final RHA revealed that there was no detectable tridymite or cristobalite in the resultant ash.

Example 2:

The RHA of Example 1 was used to prepare a 0.75 inch thick RHA filter cake by creating a slurry of RHA and DI water at a ratio fo 1 : 5. The weight of the RHA required to produce the cake was 30 grams. A No. 1 filter paper was used in a 4 inch diameter Buchner filter and an even cake resulted under 27 inches vacuum.

50 mL of DI water at a temperature of 16°C was filtered through the RHA filter cake and the through-put time was recorded. Samples of the filtered water were taken for turbidity/color analysis using Reference Basis Units (RBU) to quantify color. The RUB was evaluated by determining the intensity of the corresponding

colors at 420 nm and 720 nm using a Bauch&Lomb Model 20 spectrophotometer. The RBU value is calcuated using the following formula:

$$RBU = 1000 \left[\frac{Absorb@\lambda = 420\ nm - 2(\ Absorb\ @\lambda = 720nm)}{Cell\ width\ (cm) \times Concentration\ (gr/mL)} \right]$$

Four rice hull ashes were used. Dicalite 5000 diatomaceous earth was also used. The RHAs of the present invention were milled to create different ash sizes and are labeled RHA-1, RHA-2, and RHA-3 in the following examples. RHA-4 was supplied by another manufacturer.

Sample #	Through-put time	λ @ 420nm	λ @ 720 nm	RBU
RHA-1	59 seconds	0.008	0.008	-14.22
RHA-2	67 "	0.007	0.010	-23.11
RHA-3	53 "	0.010	0.009	-14.22
RHA-4	83 "	0.023	0.023	-40.89
DE 5000	66 "	0.007	0.007	- 8.88

In this water test, the DE produced the least turbidity, and the best through-put rate.

Example 3:

The RHA of Example 1 was used to preapre a 0.75 inch thick RHA filter cake by creating a slurry of RHA and DI water at a ratio of 1 : 5. The weight of the RHA required to produce the cake was 30 grams. A No. 1 filter paper was used in a 4 inch diameter Buchner filter and an even cake resulted under 27 inches vacuum. The four RHAs and the DE 5000 of Example 2 were used to clarify the sugar liquor described herein. Corn sugar manufactured by LD Carlson, Co., Kent, OH was dissolved in

deionized (DI) water in an amount equal to 45% solids to 55% DI weight to weight. Protein in the form of egg white was added to the corn sugar liquor in an amount equal to 26 gr/liter and heated at 85°C for 30 minutes with constant stirring. The liquor was cooled and filtered through a #170 mesh screen to remove any large egg white particles.

50 mL of sugar liquor was heated to 75°C and passed through the filter cake. The through-put time was measured. Samples of both the unfiltered and filtered sugar liquor were taken for turbidity/color analysis using Reference Basis Units (RBU) as described in Example 2.

Sample #	Through-put time	λ @ 420nm	λ @ 720 nm	RBU
RHA-1	76 seconds	0.045	0.040	-62.22
RHA-2	53 "	0.039	0.040	-72.89
RHA-3	70 "	0.037	0.039	-72.89
RHA-4	85 "	0.035	0.039	-76.00
DE 5000	88 "	0.038	0.041	-78.22
Sugar Liquor	unfiltered	0.094	0.098	-181.33

In this sugar liquor test, RHA-1 provided the best improved clarity relative to the unfiltered liquor by 191%. RHA-1 also had better filtering characteristics than the DE in terms of both clarity and filter rate.

Example 4:

The RHA filter cakes were prepared as in Example 3. The sugar liquor of Example 3 was subjected to additional heating for 40 minutes at a temperature of

85°C to increase the color. The liquor was cooled to 75°C and the RBU filter test was repeated using the four RHAs of Example 3.

Sample #	Through-put time	λ @ 420nm	λ @ 720 nm	RBU
RHA-1	90 seconds	0.062	0.059	-99.56
RHA-2	74 "	0.100	0.090	-142.22
RHA-3	86 "	0.089	0.076	-112.00
RHA-4	73 "	0.056	0.057	-103.11
Sugar Liquor	unfiltered	0.166	0.150	-238.22

In this sugar liquor test, RHA-1 provided the best improved clarity by 139%.

WHAT IS CLAIMED IS

1. A rice hull ash filter aid that contains no respirable silica in the form of cristobalite or tridymite.

2. A rice hull ash filter aid that is produced under controlled temperature conditions between 650 - 850°C.

3. A rice hull ash filter aid that can contain an amount of amorphous silica equal to 92%<AS<100%.

4. A rice hull ash filter aid that can contain an amount of activated carbon equal to 0%<AC<5%.

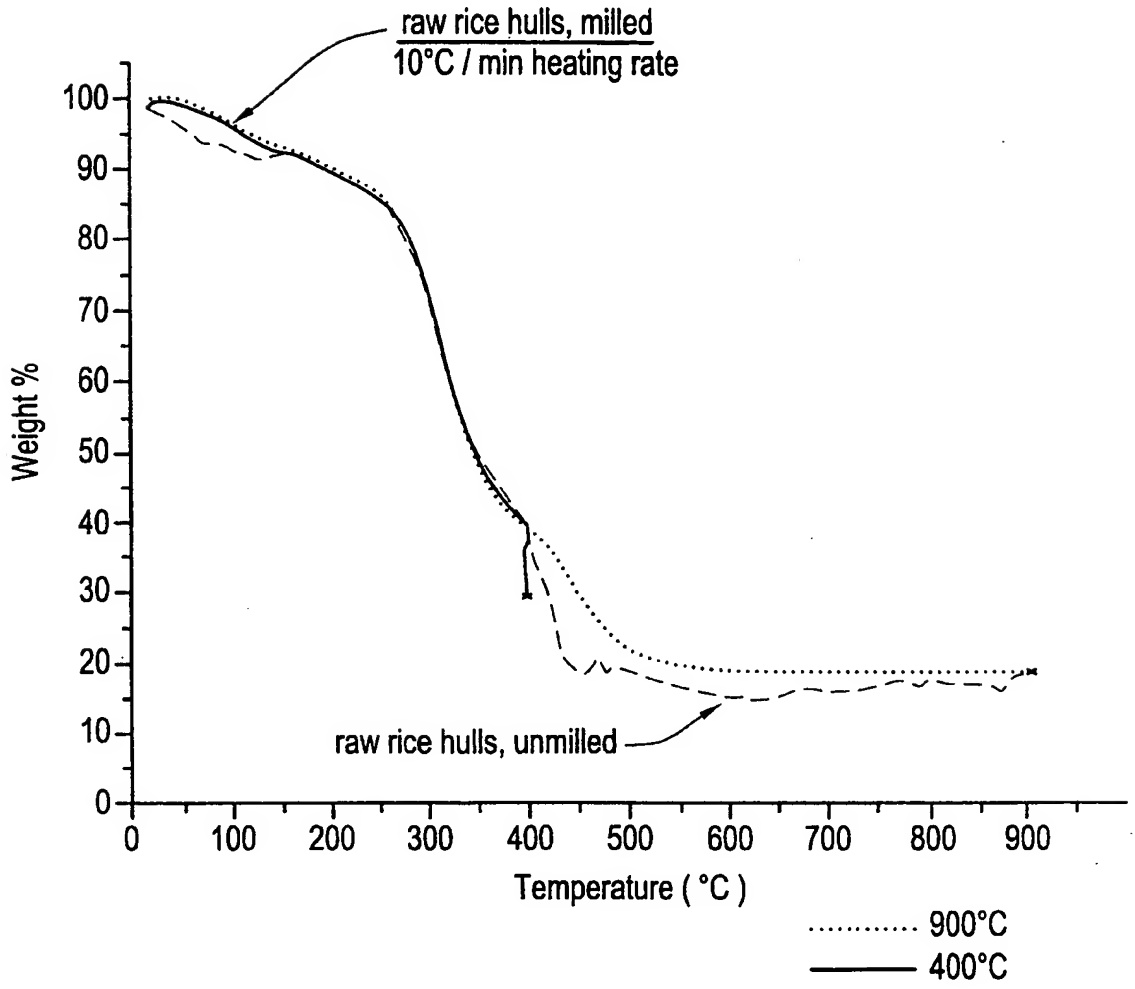
5. A rice hull ash filter aid that exhibits improved decoloring for sugar liquors.

6. A rice hull ash filter aid that exhibits improved rate of filtration for sugar liquors.

7. A rice hull ash filter aid that costs only 40% of that of DE.

FIG.1

TGA of milled and unmilled raw rice hulls



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/04134

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :B01D 39/06
US CL : 210/503
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 210/503, 500.1, 777, 917, 502/407

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,645,605 A (DURHAM) 24 February 1987, col. 3, lines 6-43; col. 6, lines 30-35.	1-7
X	US 5,595,667 A (RIEBER) 21 January 1997, abstract; col. 3, line 56 to col. 4 line 23.	1-7

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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